

Surface Tension Studies of Alkyl Esters and Epoxidized Alkyl Esters Relevant to Oleochemically Based Fuel Additives[†]

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Received April 24, 2007. Revised Manuscript Received June 26, 2007

There are several reports on the synthesis of fuel additives based on oleochemical esters, and physical data on some of these compounds is lacking. Herein, we report the surface tension of several epoxidized oleochemicals and their comparable fatty esters, at temperatures between 25 and 60 °C. Surface tensions of the olefins measured at 40 °C range from 25.9 mN m⁻¹, for isobutyl oleate, to 28.4 mN m⁻¹ for methyl linoleate. The epoxy versions of the same compounds displayed higher surface tensions of 28.1 and 32.1 mN m⁻¹, respectively. Branched ester compounds also had surface tensions between 27.4 and 30.2 mN m⁻¹. Several trends and observations were elucidated. More epoxidation or unsaturation leads to higher surface tension. Epoxidation has a larger effect on surface tension than unsaturation. Linear alkyl headgroups on fatty esters have similar surface tensions, but branched headgroups gave slightly lower surface tensions. Soy methyl esters, or epoxy soy methyl esters, give surface tensions which are between that of their two main components. Overall, the results show that all of these compounds have surface tensions which make them suitable for use as biofuel additives.

Introduction

The use of renewable resources in industrial applications has become of interest in the federal,¹ commercial,² and, most importantly, consumer^{3–5} conscience. As petroleum prices continue to remain high,⁶ use of biobased products also makes economic sense as well. Chemical producers are looking to increase their utilization of agricultural products to produce chemical feedstocks such as biobutanol,⁷ levulinic acid,⁸ and furfural,⁹ along with glycerol, a biodiesel coproduct.¹⁰

Fuel properties and the environmental impact^{11,12} of renewable oil based fuels have been well-studied.¹³ A more recent area of

interest is in the use of lubrication or fuel additives which are also based on oleochemicals.^{14–21} Because they are also vegetable oil based, these additives are likely to give the same environmental advantages as biodiesel. Epoxidation of oleochemicals has been shown to increase overall oxidative stability, and the resultant epoxides have been shown to lower overall friction, even at additive concentrations.^{15,16,22–24}

However, the effect of epoxidation on the atomization properties of oleochemically based fuels has not been studied.

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Atomization, usually considered the initial process in combustion, is a complicated process which is governed by many factors, including pressure, temperature, and injector design. Atomization phenomena have been studied in some form^{25–27} for over a century and in biodiesel for nearly 30 years.^{28–30} An equation (eq 1) used to measure the relative atomization characteristics of biodiesel and vegetable oil based fuels has been derived^{28,30} and shows the potentially important effect of surface tension on fuel properties. In one study,²⁸ it was recommended that fuel mixtures not include more than 34% vegetable oil. A more recent study shows that even low levels of monoglyceride impurities in biodiesel have a negative effect on fuel atomization and performance.²⁹ Because surface tension is an important factor in fuel properties, and epoxidized oleochemicals are potentially valuable fuel additives, a study of the surface tension of oleochemical epoxides is merited.

$$K = \left(\frac{\rho_{\text{fuel}}}{\rho_{\text{atmosphere}}} \frac{We}{Re} \right)^{1/3} \quad (1)$$

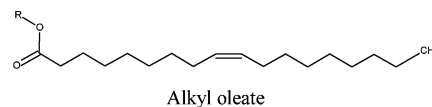
$$We \propto 1/\gamma$$

Equation 1 is used for the determination of relative atomization characteristics of a liquid (K = characteristic, ρ = density, We = Weber number, Re = Reynolds number; γ = surface tension).

Many valuable surface studies have been done on saturated fatty acids or esters,^{31–33} while much less has been reported on their unsaturated^{30,34} counterparts and none is available for epoxidized fatty ester materials. Herein, we report the surface tensions of various epoxidized oleochemicals (Figure 1), including epoxidized methyl oleate (EMO; methyl 9,10-epoxy stearate), epoxidized methyl linoleate (EMLO; methyl 9,10,12,13-diepoxy stearate), and epoxidized soybean oil methyl esters (ESME), as well as similar results for a comparable set of the parent olefins.

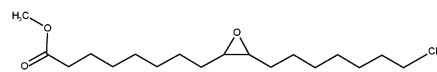
Experimental

Materials. Oleic acid (Nu chek Prep, Elsyan, MN, >99%); ethyl oleate (Nu chek Prep, Elsyan, MN, >99%); methyl linoleate (Nu chek Prep, Elsyan, MN, >99%); methyl stearate (Nu chek Prep, Elsyan, MN, >99%); hydrogen peroxide (30% Solution, Sigma-

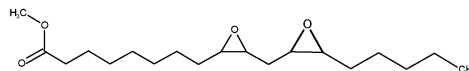


Alkyl oleate

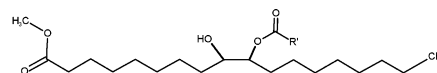
R = methyl, ethyl, propyl, butyl, isopropyl, isobutyl, 2-ethylhexyl



Epoxidized Methyl Oleate (EMO)



Epoxidized Methyl Linoleate (EMLO)



branched ester derivatives

R' = propyl, octyl, 2-Ethylhexyl, 4-oxyptenyl

Figure 1. Structures of various alkyl esters, epoxy esters, and branched esters studied herein. The R' group in the branched esters includes the carbonyl carbon as well, i.e., propyl has a total of 3 carbons in the sidechain ester.

Aldrich, St. Louis, MO, ACS reagent); formic acid (Fisher Scientific, 88%, sequencing grade); hexanes (Sigma-Aldrich, St. Louis, MO, >95%, HPLC grade); sodium chloride (Fisher, Fairlawn, NJ, ACS reagent); sodium bicarbonate (Fisher, Fairlawn, NJ, ACS reagent); sodium hydroxide (Fisher, Fairlawn, NJ, ACS reagent); sodium sulfate (Sigma-Aldrich, St. Louis, MO, 99+%, ACS reagent); propanol (Sigma-Aldrich, St. Louis, MO, 99.5% ACS reagent); 2-propanol (Sigma-Aldrich, St. Louis, MO, 99.5% ACS reagent); butanol (Fisher, Fairlawn, NJ, ACS reagent); 2-methyl-1butanol (isobutyl alcohol, Sigma-Aldrich, St. Louis, MO, 99%); octanol (Sigma-Aldrich, St. Louis, MO, ACS reagent 99%); 2-ethyl hexanol (Sigma-Aldrich, St. Louis, MO, 99+%); propionic acid (propanoic acid, Sigma-Aldrich, St. Louis, MO, 99.5%); levulinic acid (Sigma-Aldrich, St. Louis, MO, 98%); hexanoic acid (Sigma-Aldrich, St. Louis, MO, 99.5%); octanoic acid (Sigma-Aldrich, St. Louis, MO, 99%); 2-ethylhexanoic acid (Sigma-Aldrich, St. Louis, MO, 99%); and soy methyl esters (Soygold 1100, Ag. Environmental Products, Omaha, NE) were used as received.

Synthesis of Oleochemicals. Various alkyl esters which were not available commercially were synthesized by a Fischer esterification of oleic acid, which has been used previously in our laboratories.^{20,21} In summary, oleic acid (99%, 10.0 g, 35.4 mmol), the desired alcohol (ROH: methanol, ethanol, etc.) (15.0 mL), and a catalytic amount of H₂SO₄ (conc, 0.10 mL, 5.1 mol %) were combined at room temperature and then heated at reflux for 4 h. Upon cooling to room temperature, the alcohol was removed by rotary evaporation or Kugelrohr distillation and the resultant oil dissolved in hexanes (10 mL). After washing with NaHCO₃ (sat aq, 2 × 1 mL) and brine (2 × 1 mL), the organic phase was dried, filtered, concentrated, and placed for 6 h under high vacuum to afford various alkyl oleates in ~97% yield. Further characterization on the materials has been reported elsewhere.^{20,21}

Various epoxides were made by a Swern epoxidation,^{35,36} which has been modified for oleochemical use by Bunker and Wool³⁷

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Table 1. Surface Tensions of the Series of Oleochemicals Measured at 40 °C^a

| olefins | | epoxides | | branched esters ^b | |
|-----------------------------------|--------------------------------|---------------------------|--------------------------------|------------------------------|--------------------------------|
| headgroup | γ (mN m ⁻¹) | headgroup | γ (mN m ⁻¹) | sidechain ester | γ (mN m ⁻¹) |
| Me | 27.4 | Me | 27.3 | propionic | 29.1 |
| Et | 27.7 | Et | 28.3 | | |
| Pr | 27.4 | Pr | 28.0 | | |
| Bu | 27.7 | Bu | 27.9 | | |
| Oct | 27.6 | Oct | 28.6 | octanoic | 27.4 |
| IPr | 26.9 | IPr | 28.5 | | |
| IBu | 25.9 | IBu | 28.1 | | |
| 2-Ethx | 27.7 | 2-Ethx | 28.4 | 2-ethylhexanoic | 28.0 |
| methyl linoleate (2 double bonds) | 28.4 | EMLO (2 oxirane rings) | 32.1 | levulinic (4-oxypentanoic) | 30.2 |
| methyl stearate (0 double bonds) | 27.0 | ESME | 30.1 | | |
| SME (biodiesel) | 28.1 | epoxy 2-ethylhexyl soyate | 31.7 | | |

^a Me = methyl, Et = ethyl, Pr = propyl, IPr = isopropyl, Oct = octyl, IBu = isobutyl, 2-Ethx = 2-ethylhexyl, SME = soy methyl esters, ESME = epoxidized soy methyl esters. ^b From earlier work.⁴⁸

and used by our laboratory in the past.^{20,21,38} The corresponding alkyl oleate (10.0 mmol) and formic acid (88%, 25 mmol) were stirred together at 4 °C, and H₂O₂ (30% in H₂O, 20 mmol) was added slowly. The reaction proceeded at room temperature with vigorous stirring (900+ rpm). The reaction was followed by GC-MS analysis until consumption of the alkyl ester was complete (14–16 h). After removal of the aqueous phase, a portion of hexanes (20 mL) was added to the upper oily phase, which was washed with NaHCO₃ (sat aq, 2 × 5 mL) and brine (2 × 5 mL), dried, filtered, and placed for 6 h under high vacuum to provide alkyl 9,10-epoxystearates as clear oils in ~95% overall yield. Further characterization of the materials and a more detailed synthesis has been reported elsewhere.^{20,21}

Surface Tension Analysis. Surface tension measurements were taken with a Sita t60 bubble pressure tensiometer (SITA GmbH, Desden, Germany/Future Digital Scientific, Bethpage, NY) using Sita online V2.1 software. Software controlled dilutions and temperature control were handled by an Ingenieurbüro (Staufen, Germany) Cat M 26 stir plate and an Ingenieurbüro (Staufen, Germany) CAT contiburette μ -10M-C burette using Sita Labtool V1 software. They were all controlled by an IBM (White Plains, NY) Pentium 4 computer with a 3.0 GHz processor and a Windows XP operating system. A bubble lifetime of at least 4 s was used so that dynamic effects were not a factor in the measurements. This parameter was initially determined by the auto-scan function of the tensiometer. The system was calibrated using pure water with the built in calibration function on the tensiometer. The surface tensions of several organic solutions were measured, and found to agree with literature values, before the surface tension measurements of samples were undertaken.

Results and Discussion

The syntheses of the various alkyl fatty esters and oleochemical epoxides went as expected and without event, as shown in the past in our laboratories.^{20,21,39} The variety of headgroups was selected in order to study the possible effects of headgroup size and configuration on surface tension. The surface tension of each compound was measured by bubble pressure tensiometry, a method which has been shown to give results within experimental error to those obtained using more traditional tensiometry methods. The surface tensions for each of the oleochemicals was measured (Table 1) at a variety of temperatures between 25 and 60 °C with the exception of methyl

stearate, which could not be studied at 25 °C due to its solid state at that temperature. All of the samples displayed a decrease in surface tension with increasing temperature, a trend that is usually observed in organic liquids. Careful analysis of the results allowed the following trends to be elucidated.

Unsaturation. It has been known for nearly a century^{40,41} that an increase in unsaturation will significantly alter surface energies of a liquid. A relationship between the molecular volume of a liquid, its density, and its surface tension was found and labeled the MacLeod–Sugen parachor.^{42,43} From this relationship, it can be noted that the slightly less dense methyl stearate has a similar surface tension to that of methyl oleate, whereas the more dense methyl linoleate has an increased surface tension. Our measured results (Figure 2) of methyl stearate ~ methyl oleate < methyl linoleate are in agreement with values calculated in the literature.³⁰ The surface tension of a commercial biodiesel was measured, and it showed the expected behavior between methyl linoleate and methyl oleate, its two largest components.

Epoxidation. Epoxidation is expected to increase the surface tension of organic compounds, as can be appreciated by the surface tension of ethylene oxide (28.4 mN m⁻¹ at –5 °C) compared to the much lower surface tensions of ethylene (13.66 mN m⁻¹ at –88.3 °C) and ethane (16.25 mN m⁻¹ at –89.1 °C).³⁴ In oleochemicals, this effect is even larger than the effect caused by unsaturation. Oleochemicals with two epoxides have an even higher surface tension (Figure 3). This can be explained by the interactions of the oxygen containing moieties in the doubly epoxidized species forming a more stable surface structure. Measurement of the surface tension of the triply epoxidized methyl linolenate was not feasible due to its higher viscosity.

Length of Headgroup. Changes in either the size or the configuration of the alkyl headgroup in alkyl methyl esters has been shown to dramatically effect properties such as cloud point, pour point,^{20,21} and lubricity.^{44,45} The surface tensions of the methyl ester, ethyl ester, and fatty acids of many oleochemicals

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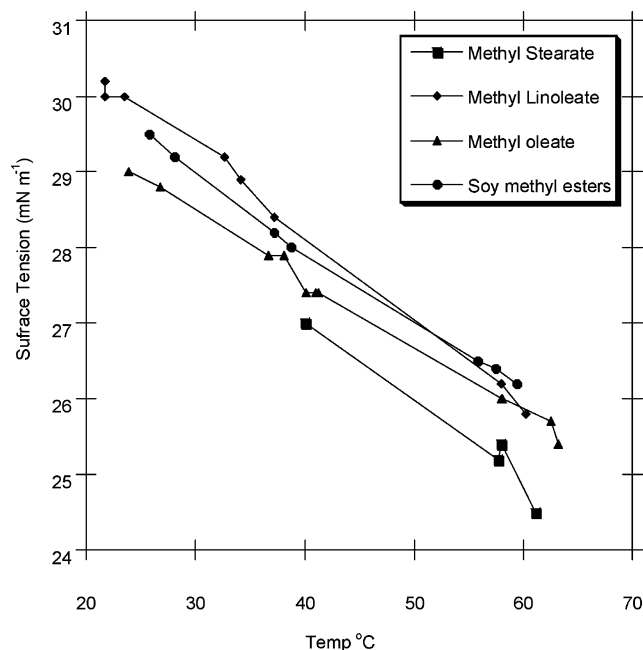


Figure 2. Plot showing the effect of increased unsaturation on the surface tension. The surface tension of commercial biodiesel (●) lies between that of its major component species, methyl oleate and methyl linoleate.

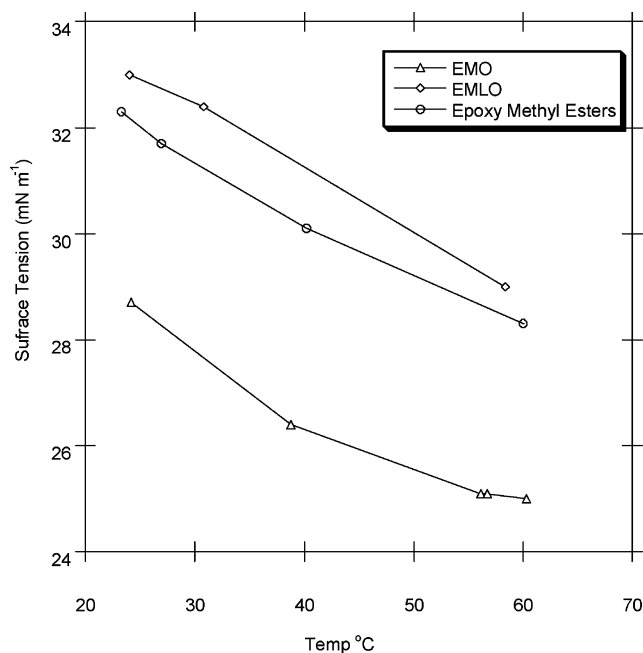


Figure 3. Plot showing the significant increase in the surface tension of oleochemicals with increased epoxidation.

have been reported,^{30–32} but not much has been done with larger headgroups. The difference between methyl and ethyl esters is quite small, always within 0.5 mN m^{-1} at 75°C . This trend is supported by our data as well, with no significant change in surface tension despite varied linear ester head groups from methyl to octyl (Figure 4). However, a significant difference was observed whenever branching was introduced into the headgroup of the compound. The branching in the headgroup, especially in the isopropyl and isobutyl ester cases, lowered the surface tension of the compounds measurably. This can be best

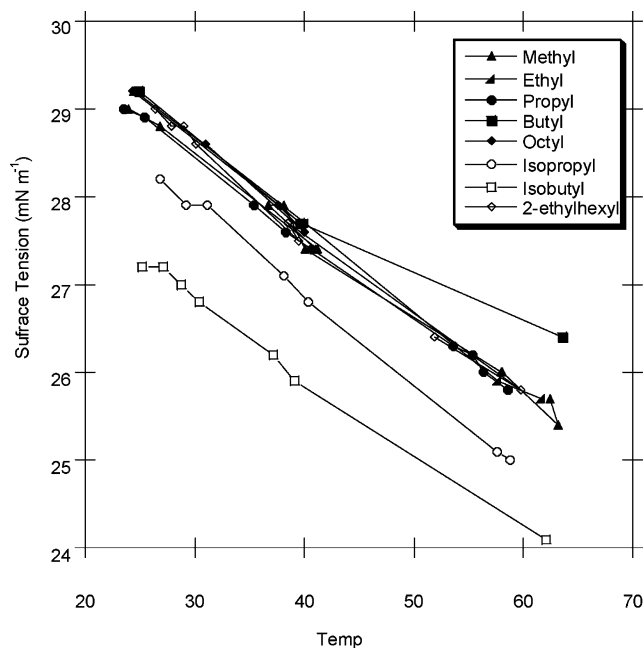


Figure 4. Plot showing the essentially negligible effect on the surface tension of alkyl esters caused by increasing the length of the ester headgroup but a significant surface tension reduction caused by branching in the headgroup.

rationalized by considering the effect of branching which disrupts the packing of the headgroups in the surface layer of the product. It is also of interest that a similar effect was not observed in the epoxy oleochemicals.

Ester Containing Sidechains. We have recently synthesized a series of compounds which contain an ester sidechain at either the 9 or 10 position of the fatty acid chain (Figure 1).^{17,46} Measurement of the surface tension of these compounds was of interest and was briefly reported earlier.¹⁷ It is of note that these compounds all have a surface tension larger than that of any of the singly epoxidized or unsaturated compounds, but all have a lower surface tension than the double epoxidized EMLO. This points to the important effect of the oxygenated moiety in the surface tension phenomena.

Conclusion

The physical structure of an oleochemical has a large impact on its observable surface properties. As well as the studies herein on ester chain length and branching, studies on potential additives with dimeric or polymeric structures, or those containing other moieties, such as carbonates, are of interest. Within the current study, several basic trends were observed. First, increasing unsaturation in the fatty chain of an oleochemical causes competing effects and leads to greater surface tension in methyl linoleate than in the other methyl esters studied. Second, the headgroup length does not greatly affect surface tension, but branches in the headgroup lower it significantly. Finally, oxygen containing moieties, such as epoxides or sidechain esters, effect the surface properties more than unsaturation, with the doubly epoxidized EMLO having the highest surface tension of any of the compounds studied.

Overall, the magnitude of the surface tension changes is fairly small, with a difference of only about 4 mN m^{-1} in the highest and lowest measurements at 40°C . This leaves even the highest

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compound measured herein, EMLN, about 4 mN m^{-1} lower than the observed surface tension of soybean oil (35.6 mN m^{-1} at 38°C) or peanut oil (34.5 mN m^{-1} at 38°C).⁴⁷ From these results, the amount of our compounds that could be added to a mixture of diesel is considerably greater than the 0–34% range that is advisable for straight vegetable oil.³⁸ At least from an atomization standpoint, the surface tensions should allow the blending of our components to any level that was economically feasible. A broader conclusion is that any impurities forming in biodiesel, of this type of oxidized ester structure, should have

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minimal or no effect on the atomization performance of a fuel. This is evidence that any of the negative atomization effects demonstrated by Allen and Watts,²⁹ for glyceride impurities in biodiesel, are probably not originating from a surface tension effect. The small surface tension change is probably only sufficient to cause little if any change in the atomization characteristics of a fuel. Good news for those wanting consistent behavior when using oleochemically based fuel additives.

Acknowledgment. We would like to acknowledge Ms. Donna I. Thomas for surface tension measurements.

EF700213Z